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Reaction of Atomic Hydrogen with Hydrogenated Porous Silicon - Detection of Precursor
to Silane Formation

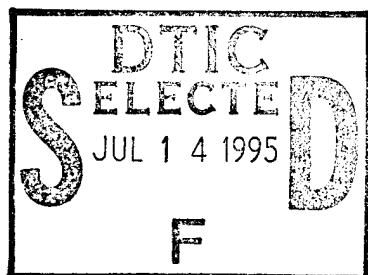
by

John A. Glass Jr., Edward A. Wovchko, and John T. Yates, Jr.

Submitted To

Surface Science

Surface Science Center
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16 June 1995

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13. ABSTRACT (Maximum 200 words)

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Abstract

The reaction of electrochemically formed porous silicon with atomic hydrogen or atomic deuterium has been studied at cryogenic temperatures and at room temperature.

Cryogenic temperatures were chosen in order to kinetically suppress silane formation (silicon etching) and to spectroscopically observe the surface precursor to SiH_4 formation. By comparing developments in the Si-H and Si-D stretching mode regions of the infrared spectrum, it is demonstrated that SiH_3 is stabilized at 133 K without formation of SiH_4 (g). Warming to near 200 K and above evolves SiH_4 (g) as SiH_3 reacts with neighbor SiH_x species. It is demonstrated that the reaction $\text{SiH}_3 + \text{H} \rightarrow \text{SiH}_4$ (g) does not proceed rapidly at 133 K. This suggests that disproportionation of SiH_3 and SiH_x surface species to make SiH_4 (g) dominates in the etching process on porous silicon at lower temperatures.

I. Introduction

The capability of atomic hydrogen to passivate and to etch silicon surfaces has led to many important investigations of the silicon/hydrogen system. A number of surface techniques, both structural and chemical, have been applied to study hydrogen on both crystalline and amorphous silicon surfaces [1-29]. These studies show that both crystalline and amorphous silicon can be passivated by chemisorbed hydrogen as dangling bonds are capped. This hydrogen may either be deposited during the formation of silicon films as is the case for SiH_4 decomposition to form amorphous silicon, or may be readily added as is the case for crystalline silicon when it is reacted with $\text{HF}(\text{aq})$ or with atomic hydrogen. The chemisorbed hydrogen placed on crystalline silicon either by $\text{HF}(\text{aq})$ treatment or by atomic hydrogen exposure has been identified as consisting of mono (Si-H), di (Si-H_2) and tri (Si-H_3) hydride surface species [1, 6, 17].

Crystalline silicon can be etched by reaction with atomic hydrogen at low temperatures. This etching process is postulated to proceed by desorption of SiH_4 produced from $\text{SiH}_3(\text{a})$ and $\text{SiH}_x(\text{a})$ surface species at or above 200K [4, 7, 8, 9, 16] and by desorption of a small amount of higher silanes (Si_2H_6 and Si_3H_8) [17]. Porous silicon, however, an electrochemically produced hybrid between crystalline and amorphous silicon, has been less well studied with regard to reactivity with atomic hydrogen. Only the thermal desorption of hydrogen from the electrochemically etched material has been studied [19]. Therefore, in order to gather more information concerning hydrogen interactions on porous silicon, we have studied the reaction of atomic hydrogen with hydrogenated porous silicon by Fourier Transform Infrared Spectroscopy (FTIR) in transmission through the porous layer. By working at cryogenic temperatures, we have been able to suppress the etching reaction forming silane, and to trap and spectroscopically monitor the key intermediate surface species in the etching reaction.

II. Experimental

A. Porous Silicon Preparation

Si(100) single crystals (Virginia Semiconductors Limited) used in this study were 1.3 cm x 1.3 cm x 0.15 cm p-type B doped (5-10 Ω cm) crystals. The detailed preparation of the porous silicon was as previously described [30]. Each crystal was slotted on its edges, cleaned (RCA cleaning [31]), and electrochemically etched at 100 mA for 20 sec in a homogenous mixed, de-oxygenated solution of 48% HF (aq) and anhydrous $\text{CH}_3\text{CH}_2\text{OH}$. The crystal was then dipped into 48% HF (aq) for 15 seconds to remove any native surface oxide and any residual contamination. This procedure leads to a highly hydrogenated silicon surface. Each crystal was then dried and stored in a dry and clean environment until mounting in the infrared cell.

B. Infrared Cell

All experiments were conducted in a special infrared cell shown in Figure 1. The main body (left of the radiation shield) of the cell has been described in detail previously [30], and is based upon an earlier design [30, 32]. A stainless steel cube holds a rotatable Dewar (Thermonics rotary seal, not shown) with electrical and thermocouple feedthroughs, two differentially pumped KBr optical windows, a tungsten filament atomic hydrogen source, and a gas/vacuum line connection. The crystal, being mounted at the end of the rotary seal, was temperature controlled by a Chromel / Alumel, type K, thermocouple isolated from the silicon in an edge slot by a tantalum foil shield and connected to a Honeywell UDC 500 digit temperature controller and a custom built 0-50A, 0-100V power supply. Cooling was achieved using $\text{N}_2(\text{l})$ in the Dewar.

Temperatures could be maintained to within ± 2 K in the range of 120 K to 900 K. The system was pumped in sequence with a $\text{N}_2(\text{l})$ -cooled zeolite sorption pump, a 50 L/s Balzers turbomolecular pump, and a Varian 20 L/s ion pump. Base pressures in this system were typically $< 1 \times 10^{-8}$ Torr after 20 hours of evacuation. In addition to the pumps, the vacuum system contained a UTI Model 100C quadrupole mass spectrometer for leak detection and gas analysis and a capacitance manometer (0-1000 Torr) for accurate pressure measurements.

The atomic hydrogen source (right of the radiation shield) consisted of a heavy stainless steel cylinder with copper tubing tightly wrapped in a helical slot around the outside for cooling, a quartz wall shield, and an opaque quartz radiation shield. Placed within this shielded region was a 0.025 cm diameter tungsten filament which could be heated by a 0-50A, 0-100 V AC power supply to ~ 2000 K as determined by an optical pyrometer. Atomic hydrogen produced at the hot filament is reflected by the outer quartz shield and enters the main infrared cell by passage through the space between the edges of the rectangular radiation shield and the outer quartz shield. Radiation heating of the crystal due to the tungsten filament was minimized by the radiation shield and the small heating effect observed was compensated automatically by the temperature controller.

C. Infrared Measurements

All infrared spectra were recorded using a nitrogen-purged Mattson Research Series I Fourier transform infrared spectrometer. Data were processed and manipulated using Mattson Fourier Infrared Software Tools (FIRST). The spectrometer was equipped with a liquid nitrogen cooled HgCdTe detector and was capable of obtaining spectra from 4000 - 500 cm^{-1} . In this study spectra were measured by averaging 1024 scans at a spectral resolution of 2 cm^{-1} . All spectra were recorded at 133 K and either under evacuation, or, as was the case for adsorbed SiH_4 and SiD_4 , under 2 mTorr of silane

pressure. Absorbance spectra were obtained by ratioing single beam spectra of the sample plus the window with single beam spectra through the window alone.

D. Materials and Exposures

Hydrogen (H_2) (Matheson - 99.9995%) and Silane (SiH_4) (Matheson - 99.999%) were used directly from the cylinder without further purification. Deuterium (D_2) (Matheson 99.82%) and Deutero-Silane (SiD_4) (Matheson - 99.99%) used in this study were transferred from a cylinder to pre-evacuated and baked glass bulbs prior to use. For each exposure of atomic hydrogen, fresh hydrogen or deuterium gas was placed into the cell at pressures of 1-40 mTorr. The tungsten filament was then heated to ~ 2000 K for 1-2 minutes for each exposure. Additional exposures resulted in total atomic hydrogen exposures up to 20 min. in duration.

III. Results

A. Electrochemically Produced Hydride Surface.

Following electrochemical formation of the porous silicon layer, the Si-H region of the infrared spectrum, Figure 2, exhibited absorption bands centered at 2091 cm^{-1} , 2115 cm^{-1} , and 2141 cm^{-1} . These Si-H frequencies were assigned as follows: 2091 cm^{-1} - SiH_2 ; 2115 cm^{-1} - SiH ; and 2141 cm^{-1} - SiH_3 [1, 6, 18, 19, 26].

B. Reaction of Hydrogenated Surface with Atomic D and Atomic H at 133 K

Figures 3 and 4 show the reactions of atomic deuterium and atomic hydrogen with a porous silicon surface at 133 K. For both atomic deuterium and atomic hydrogen

exposure, the Si-H region of the spectrum behaves almost identically. The feature at 2141 cm^{-1} (SiH_3) increased in intensity, broadened, and shifted to 2144 cm^{-1} and both the SiH_2 (2091 cm^{-1}) and SiH (2115 cm^{-1}) features decreased in intensity. The Si-D region, however, showed markedly different results. In the atomic deuterium experiment three new features developed at 1570 , 1550 , and 1541 cm^{-1} , whereas in the atomic hydrogen experiment no features were observed in the Si-D region, as would be expected.

C. Heating Experiments

Annealing experiments on the porous silicon surface following the reaction with atomic deuterium are displayed in Figure 5. All of the spectroscopic features produced from the atomic deuterium exposure in both the Si-D and the Si-H spectral regions decreased significantly upon warming to 298 K . This decrease back to the original spectrum for the porous silicon begins at 153 K and is essentially complete by 213 K . Examination of the Si-H region following warming to 298 K shows that all three features, 2091 cm^{-1} - SiH_2 , 2115 cm^{-1} - SiH , and 2141 cm^{-1} - SiH_3 , exhibit a decrease in intensity from their original values after exposure to atomic deuterium at 133 K . Mass spectrometric analysis of the gas phase thermal products showed the presence of the etching products, $\text{SiH}_x\text{D}_{4-x}$ ($x=1$ to 4), $\text{Si}_2\text{H}_x\text{D}_{6-x}$ ($x=1$ to 6 ; $<1\%$ as compared with silane maximum), and $\text{Si}_3\text{H}_x\text{D}_{9-x}$ ($x=1$ to 9 ; $<0.1\%$ as compared with silane maximum)

D. Control Experiments with SiH_4 and SiD_4

In Figure 6 a spectral comparison is made between SiH_4 (a) on porous silicon and the products of the atomic hydrogen - porous silicon reaction as observed in the Si-H stretching region. The SiH_4 (a) feature located at 2171 cm^{-1} does not correspond to any of the SiH_x surface features observed in the atomic hydrogen reaction at a surface

temperature of 133 K. Also, in Figure 6 a spectral comparison is made between SiD_4 (a) on porous silicon and the reaction products of the atomic deuterium - porous silicon reaction as observed in the Si-D stretching region. Similarly, the SiD_4 (a) feature located at 1584 cm^{-1} does not correspond to any of the SiD_x features observed in the atomic deuterium reaction at 133 K.

B. Reaction of Hydrogenated Surface with Atomic D at 298 K

Figure 7 shows the SiH and SiD infrared regions for the reaction of atomic deuterium with hydrogenated porous silicon at 298 K. All three bands in the Si-H region, 2091 cm^{-1} , 2115 cm^{-1} , and 2141 cm^{-1} , decrease uniformly in intensity and without shifting in frequency. The Si-D infrared region, surprisingly, shows no development of infrared features.

IV. Discussion

A. Assignment of Surface Hydrogenated Modes

Electrochemical etching of the Si(100) surface results in a pore structure in which the surface silicon atoms are covered with hydrogen. The assignment of the Si-H features at 2091 cm^{-1} , 2115 cm^{-1} , and 2141 cm^{-1} has been a subject of much debate in the literature [1, 6, 30, 33]. Chabal [1,6] and Chazalviel [33] have assigned the features to Si-H stretching modes for SiH (2091 cm^{-1}), SiH₂ (2115 cm^{-1}), and SiH₃ (2141 cm^{-1}) based on internal reflection infrared measurements and calculational studies of Si(100), and Si(111) crystals [1,6] and porous silicon samples[33]. George, in contrast, suggests the assignments should be SiH₂, SiH, and O_xSiH_x, respectively for these three spectroscopic

features, based upon thermal annealing and transmission infrared measurements of porous silicon[19]. Our assignments correspond to that of George for the two lower frequency features but follow Chabal and Chazalviel's work for the high frequency feature.

Therefore we assign the Si-H region as follows: 2091 cm^{-1} - SiH_2 , 2115 cm^{-1} - SiH , and 2141 cm^{-1} - SiH_3 .

B. Reaction of Hydrogenated Porous Silicon with Atomic Hydrogen (Deuterium)

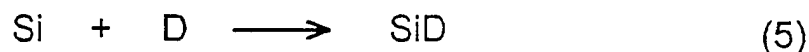
The results of the reaction of atomic hydrogen and atomic deuterium with hydrogenated porous silicon are shown in Figures 3 and 4. The intensity increase and frequency shift to 2144 cm^{-1} of the feature at 2141 cm^{-1} , which is observed in both experiments, is believed to be due to the formation of $\text{SiH}_x\text{D}_{3-x}$ ($x=1$ to 3) surface species. This assignment is based upon the location and assignments detailed above for the electrochemically etched porous silicon layer. This $\text{SiH}_x\text{D}_{3-x}$ ($x=1$ to 3) species would be produced from the following reactions:



The fact that both atomic hydrogen and atomic deuterium produce essentially the same spectral developments in the Si-H region can be rationalized if SiH_2D , and SiD_2H , and SiH_3 exhibit very similar vibrational frequencies in the Si-H region; these frequencies are unresolved on porous silicon. Indeed, as may be seen in Table I, the Si-H modes in the

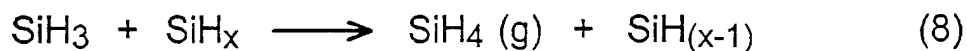
various D-substituted silane species span a range of only 14 cm^{-1} . The shift from 2141 cm^{-1} to 2144 cm^{-1} after atomic hydrogen or atomic deuterium attack may be due to breakage of large numbers of back bonds within the porous layer or to isotopic effects. Shifts to higher frequency have been observed in the case of amorphous silicon when the sample is prepared with a large concentration of hydrogen within the material (small number of back bonds) [34]. In addition to the formation of $\text{SiH}_x\text{D}_{3-x}$ ($x=1$ to 3) species, reactions 1 through 4 would also cause a decrease in the coverage of SiH_2 and SiH surface species. This was observed for the atomic deuterium and to a lesser extent for the atomic hydrogen experiment resulting in a decrease in Si-H mode intensity at 2115 cm^{-1} and 2091 cm^{-1} . The lack of observable quantities of either gas phase or surface phase monosilane (See Thermal Behavior section below), $\text{SiH}_x\text{D}_{4-x}$ ($x=1$ to 4), produced from the reaction of SiH_3 surface species with atomic hydrogen at 133 K is unexpected since the SiH_3 surface species should be susceptible to atomic hydrogen (deuterium) attack. However, spectroscopic evidence showing the lack of general depletion of the SiH and SiH_2 infrared intensities and the conversion of lower surface SiH_x species to SiH_2D and SiHD_2 species under extensive deuterium exposure, suggests that significant etching (silane formation) of the porous silicon surface by atomic H(D) at 133 K does not occur.

The three poorly resolved infrared features which develop in the Si-D region upon exposure of the hydrogenated porous silicon surface to atomic deuterium at 133 K are tentatively assigned as SiD_3 , SiHD_2 , and SiH_2D surface species. These assignments are based upon the thermal behavior of the surface species giving the three bands at 1570 cm^{-1} , 1550 cm^{-1} , and 1541 cm^{-1} (See Thermal Behavior section below). In addition, the frequency range (29 cm^{-1}) for the three Si-D region modes is comparable to the 28 cm^{-1} frequency range of the various deuterated silanes, SiH_3D to SiD_4 in the Si-D region (See Table I). Presumably, SiD_3 is produced by reactions (5)-(7) where new Si sites are produced in reactions (6) and (7) by back bond attack.

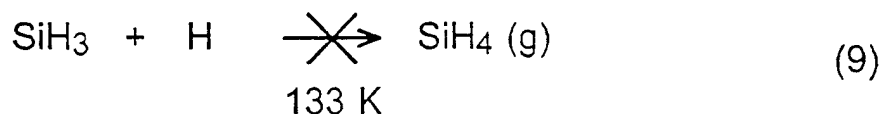


C. Thermal Behavior of Hydrogenated Porous Silicon following Reaction with Atomic D

A very surprising result was obtained following heating of the hydrogenated porous silicon surface which had been subjected to attack by atomic deuterium. Figure 5 shows that essentially all surface species containing deuterium are removed by heating to 213 K, and complete removal of these species occurs by 298 K, as shown in Figure 5. Here a large fraction of the $\text{SiH}_x\text{D}_{3-x}$ ($x=0$ to 2) species (2144 cm^{-1} , 1570 cm^{-1} , 1550 cm^{-1} and 1541 cm^{-1}) and a smaller fraction of SiH (2115 cm^{-1}), SiH_2 (2091 cm^{-1}) and SiH_3 (2141 cm^{-1}) species disappear as deuterated silane species ($\text{SiH}_x\text{D}_{4-x}$ ($x=1$ to 4)) are evolved. These results suggest that $\text{SiH}_x\text{D}_{3-x}$ ($x=0$ to 2) species act as a precursors to silane production ($\text{SiH}_x\text{D}_{4-x}$ ($x=1$ to 4)) by a reaction with SiH_x ($x=1$ to 3) surface species in the range of 153 K - 213 K. This reaction, generalized for atomic hydrogen, would involve the reaction of SiH_3 with SiH_x as detailed in reaction (8).



In contrast, the reaction involving direct atomic hydrogen (deuterium) attack on SiH_3 surface species appears not to occur extensively (reaction (9)) at 133 K.



Extensive exposure of the hydride surface to atomic deuterium does not cause a general depletion of Si-H infrared intensity, but instead causes the conversion of lower hydride species to SiH_2D and SiHD_2 species, at which point the reaction stops. Reaction (8) is consistent with previous hypotheses [4, 7, 8, 9, 16] where SiH_4 , desorbing at ~ 200 K, was postulated to originate via reaction (8). Our results confirm reaction (8) by direct spectroscopic observation of the thermal behavior of the SiH_3 species and its deuterated versions. The small amounts of higher silanes formed in etching were consistent with literature analysis on single crystals [17] and represented only a small fraction of the total etching products. In addition, these experiments show clearly that a mechanism involving the formation of a trapped SiH_4 (SiD_4) species at 133 K on the porous silicon surface is untenable, as shown by the experiment in Figure 6.

D. Reaction of Hydrogenated Porous Silicon with Atomic Deuterium at 298 K

In contrast to the reaction at 133 K, the reaction of atomic deuterium with hydrogenated porous silicon at 298 K, Figure 7, showed only a rapid loss of the SiH infrared band intensities at 2091, 2115, and 2141 cm^{-1} and no production of SiD infrared bands. These data are consistent with the thermal annealing experiments of the surface which has been hydrogenated at 133 K. Here we observed the loss of all the $\text{SiH}_x\text{D}_{3-x}$ ($x = 0$ to 2) species intensity and a smaller loss of the SiH_x ($x = 1$ to 3) intensities by reaction (8) at 298 K. The lack of the presence of SiD bands in the infrared spectrum suggests that the rate of surface exchange of hydrogen and deuterium on the porous silicon surface at 298 K is slow compared to the rate of etching reaction, and that probably reaction (8) is still dominating the etching process at 298 K.

Estimation of the etching rate at 298 K based upon the behavior of the infrared spectrum during atomic deuterium etching and the depth of the porous layer calculated from the electrochemical etching time showed an etch rate of ~ 0.03 $\mu\text{m}/\text{min}$. at a

hydrogen pressure of 10 mTorr. This value is consistent with other etching experiments on single crystals [16] and shows that the porous silicon surface still resembles a single crystal surface [19] in so far as its etching rate in atomic hydrogen is concerned.

V. Conclusions

The following conclusions regarding the etching mechanism of porous silicon by atomic hydrogen have been reached using infrared spectroscopy to study the various surface hydrogenated species.

- (1) Hydrogenated porous silicon exhibits Si-H infrared frequencies corresponding to SiH_3 , SiH_2 and SiH surface species.
- (2) Exposure of hydrogenated porous silicon to either atomic hydrogen or atomic deuterium indicates that additional silicon trihydride surface species are produced at 133 K. At this temperature, isotopic exchange is not observed.
- (3) Exposure of hydrogenated porous silicon to atomic deuterium at 133 K followed by annealing to 298 K shows that etching of the surface occurs without formation of a stable Si-D surface species. Similar results are obtained during atomic deuterium exposure to hydrogenated porous silicon at 298 K.
- (4) Etching proceeds from a precursor trihydride surface species to silane through a disproportionation reaction with neighboring SiH_x surface species at 153 - 298 K. Small amounts (<1%) of higher silanes were detected following heating.
- (5) Surface SiH_3 species do not react with atomic hydrogen at 133 K.

IV. Acknowledgments

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References

1. Y.J. Chabal, G.S. Higashi, K. Raghavachari, and V.A. Burrows, *J. Vac. Sci. Technol. A* 7 (1989) 2104.
2. M. Niwano, Y. Kimura, and N. Miyamoto, *Appl. Phys. Lett.* 65 (1994) 1692.
3. M. Niwano, J. Kageyama, K. Kurita, K. Kinashi, I. Takahashi and N. Miyamoto, *J. Appl. Phys.* 76 (1994) 2157.
4. C.C. Cheng, and J.T. Yates Jr., *Phys. Rev. B* 43 (1991) 4041.
5. D.D. Koleske, S.M. Gates, and J.A. Schultz, *J. Chem. Phys.* 99 (1993) 5619.
6. Y.J. Chabal, and K. Raghavachari, *Phys. Rev. Lett.* 54 (1985) 1055.
7. C.M. Greenlief, S.M. Gates, and P.A. Holbert, *J. Vac. Sci. Technol. A* 7 (1989) 1845.
8. D.R. Olander, M. Balooch, J. Abrefah, and W.J. Siekhaus, *J. Vac. Sci. Technol. B* 5 (1987) 1404.
9. H. Kobayashi, K. Edamoto, M. Onchi, and M. Nishijima, *J. Chem. Phys.* 78 (1983) 7429.
10. C.T. Kao, L.H. Dubois, and R.G. Nuzzo, *J. Vac. Sci. Technol. A* 9 (1991) 228.
11. H. Wagner, R. Butz, U. Backes, and D. Bruchmann, *Solid State Commun.* 38 (1981) 1155.
12. P.J. Chen, M.L. Colaianni, and J.T. Yates, Jr., *J. Appl. Phys.* 70 (1991) 2954.
13. K. Sinniah, M.G. Sherman, L.B. Lewis, W.H. Weinberg, J.T. Yates, Jr., and K.C. Janda, *J. Chem. Phys.* 92 (1990) 5700.
14. M.J. Bozack, W.J. Choyke, L. Muehlhoff, and J.T. Yates, Jr. *J. Appl. Phys.* 60 (1986) 3750.
15. S.M. Gates, R.R. Kunz, and C.M. Greenlief *Surf. Sci.* 207 (1989) 364.
16. J. Abrefah, and D.R. Olander *Surf. Sci.* 209 (1989) 291.

17. K. Okamoto, M. Shinohara, T. Yamanishi, S. Miyazaki, and M. Hirose Applied Surface Science 79/80 (1994) 57.
18. W.X. Zhu, X.Y. Gao, L.Z. Zhang, J.C. Mao, B.R. Zhang, J.Q. Duan, and G.G. Qin, Superlattices and Microstructures 12 (1992) 409.
19. P. Gupta, V.L. Colvin, and S.M. George, Phy. Rev. B. 37 (1988) 8234.
20. Japan Annual Reviews in Electronics Computers & Telecommunications: Amorphous Semiconductor Technologies & Devices 1982, Y. Hamakawa Ed., (North-Holland, New York, 1981) pp. 62-65.
21. Properties of Amorphous Silicon, M.H. Brodsky Ed., (INSPEC - EMIS Data reviews no. 1, 1985) pp 4.1-4.12.
22. A. Madan and M.P. Shaw, The Physics and Applications of Amorphous Semiconductors (Academic Press, New York, 1988) pp. 30-35.
23. P. John, I.M. Odeh, and M.J.K. Thomas, Solid State Commun. 41 (1982) 341.
24. H. Wagner, and W. Beyer, Solid State Commun. 48 (1983) 585.
25. T. Imura, K. Mogi, A. Hiraki, S. Nakashima, and A. Mitsuishi, Solid State Commun. 40 (1981) 161.
26. G. Lucovsky, S.S. Chao, J. Yang, J.E. Tyler, and W. Czubatyl, J. Vac. Sci. Technol. A 2 (1984) 353.
27. M. H. Brodsky, M. Cardona, and J. J. Cuomo, Phy. Rev. B 16 (1977) 3556.
28. P. John, I.M. Odeh, M.J.K. Thomas, M.J. Tricker, and J.I.B. Wilson, Phys. Stat. Sol. 105 (1981) 499.
29. G. Lucovsky, Solid State Commun. 29 (1979) 571.
30. J.A. Glass, Jr., E.A. Wovchko, J.T. Yates, Jr., Surf. Sci. Accepted for publication.
31. W. Kern and D.A. Puotinen, RCA Rev. 31 (1970) 187.
32. P. Basu, T.H. Ballinger and J.T. Yates, Jr., Rev. Sci. Instrum. 59 (1988) 1321.

33. Venkateswara Rao, A. Ozanam, F., and Chazalviel, J.N. J. Electrochem. Soc. 138 (1991) 153.
34. Lucovsky, G. J. Vac. Sci. Technol. 16 (1979) 1225.
35. Wilde, R.E. Srinivasan, K.K Harral, R.W. and Sankar, S.G. J. Chem. Phys. 55 (1971) 5681.

Figure Captions:

- Figure 1: Infrared cell containing atomic hydrogen source attachment.
- Figure 2: Silicon hydride stretch region following porous silicon formation from electrochemical etch.
- Figure 3: Silicon hydride and silicon deuteride infrared stretch region following atomic deuterium exposure at 133 K.
- Figure 4: Silicon hydride and silicon deuteride infrared stretch region following atomic hydrogen exposure at 133 K.
- Figure 5: Annealing of hydrogenated silicon after exposure to atomic deuterium at 133 K.
- Figure 6: Comparison between $\text{SiH}_4(\text{a})$ and $\text{SiD}_4(\text{a})$ on porous silicon and the corresponding atomic hydrogen or deuterium experiment with hydrogenated porous silicon.
- Figure 7: Silicon hydride and silicon deuteride infrared stretch region following atomic hydrogen exposure at 298 K.

Table I: Infrared frequencies for Argon matrix isolated $\text{SiH}_x\text{D}_{4-x}$ ($x=1$ to 4), SiH_4 and SiD_4 on porous silicon, and atomic hydrogen / deuterium reactions with hydrogenated porous silicon.

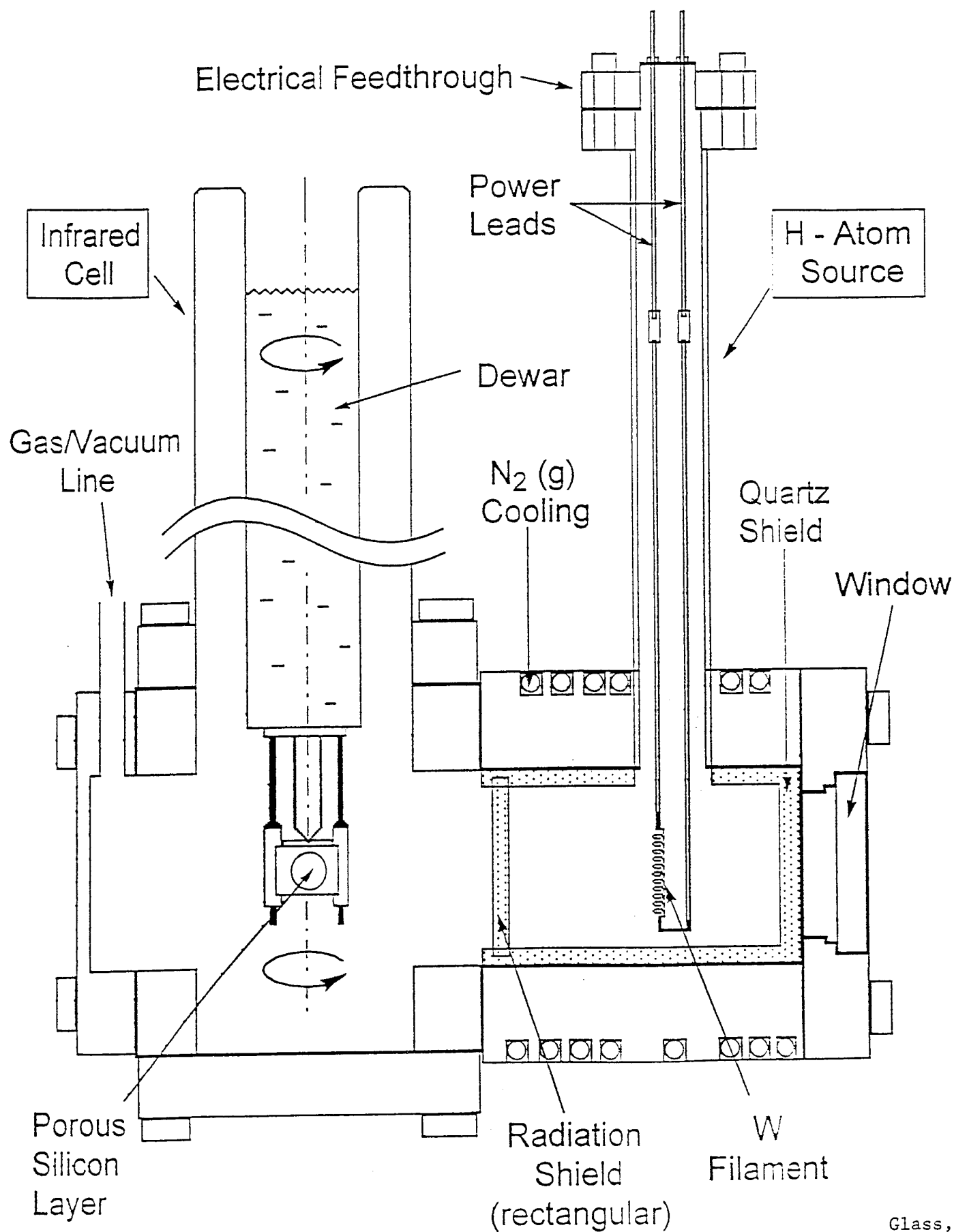
Molecule	Si-H Infrared Frequency cm^{-1}	Si-D Infrared Frequency cm^{-1}
SiH_4^{a}	2176	-
$\text{SiH}_3\text{D}^{\text{a}}$	2176	1584
$\text{SiH}_2\text{D}_2^{\text{a}}$	2175	1591 1571
SiHD_3^{b}	2189	1599
SiD_4^{a}	-	1584
SiH_4 on porous Silicon ^c	2171	-
SiD_4 on porous silicon ^c	-	1584
Atomic H on porous silicon ^c	2144	-
Atomic D on porous silicon ^c	2144	1570 1550 1541

a. Reference 31.

b. Neon matrix, No Argon matrix data available. Reference 31.

c. This work.

Infrared Cell and Atomic Hydrogen Source

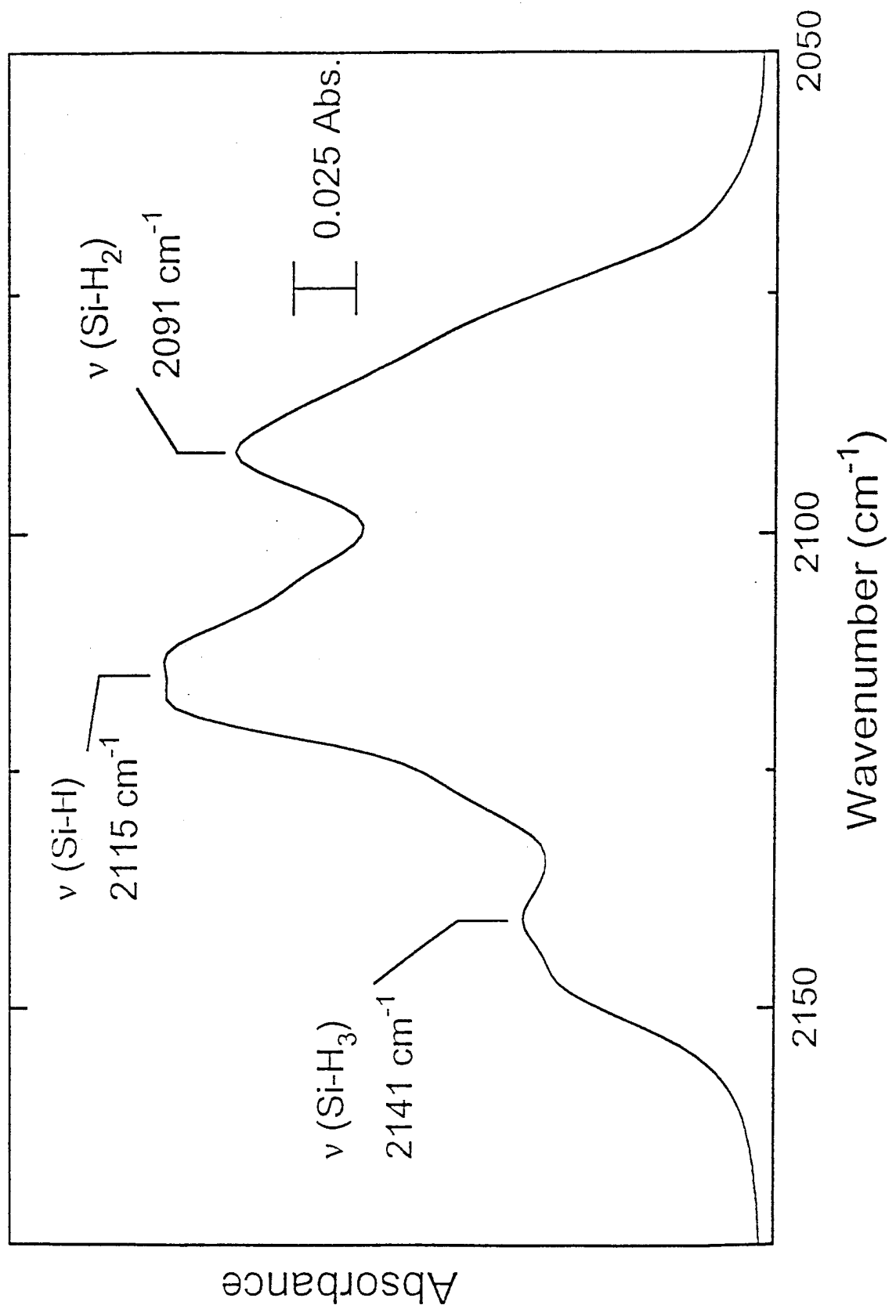


Glass, et al.

Figure 1

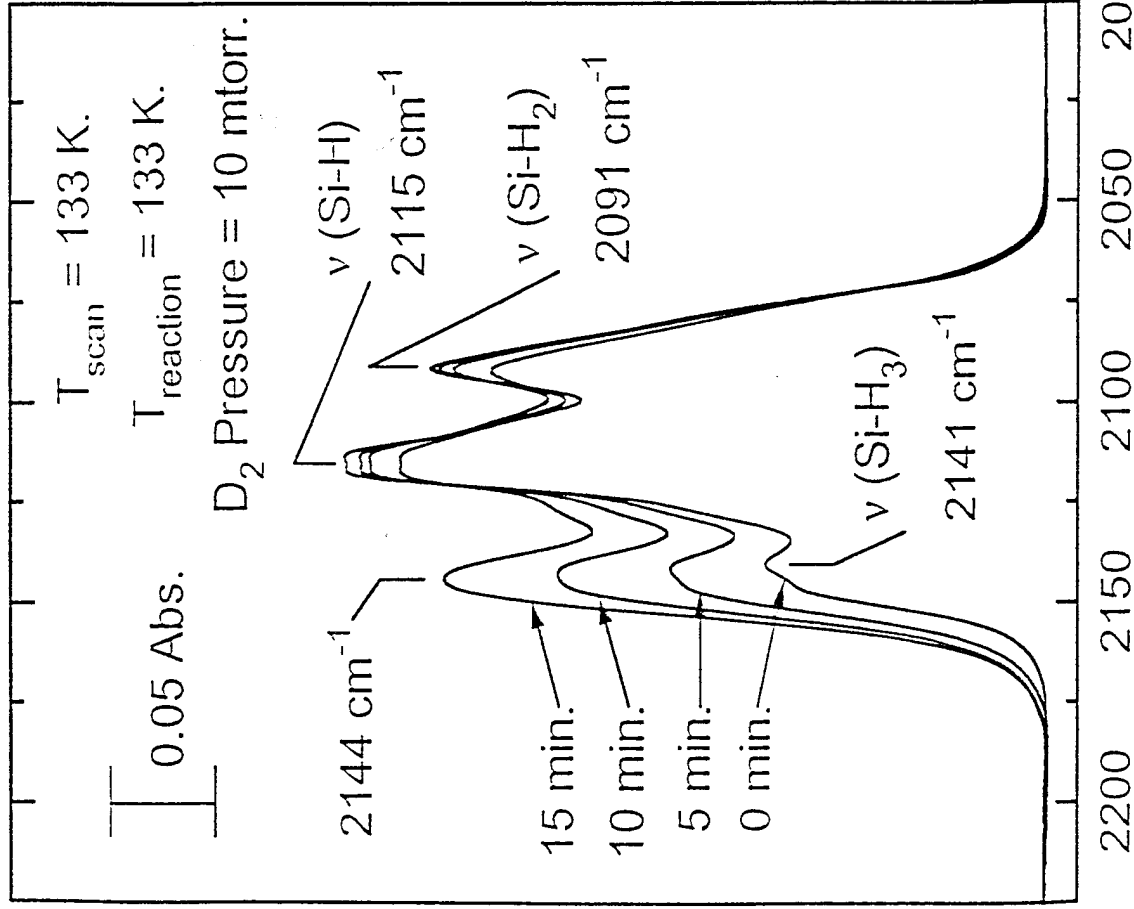
Fig 2

SiH_x Species after
Electrochemical Etch.

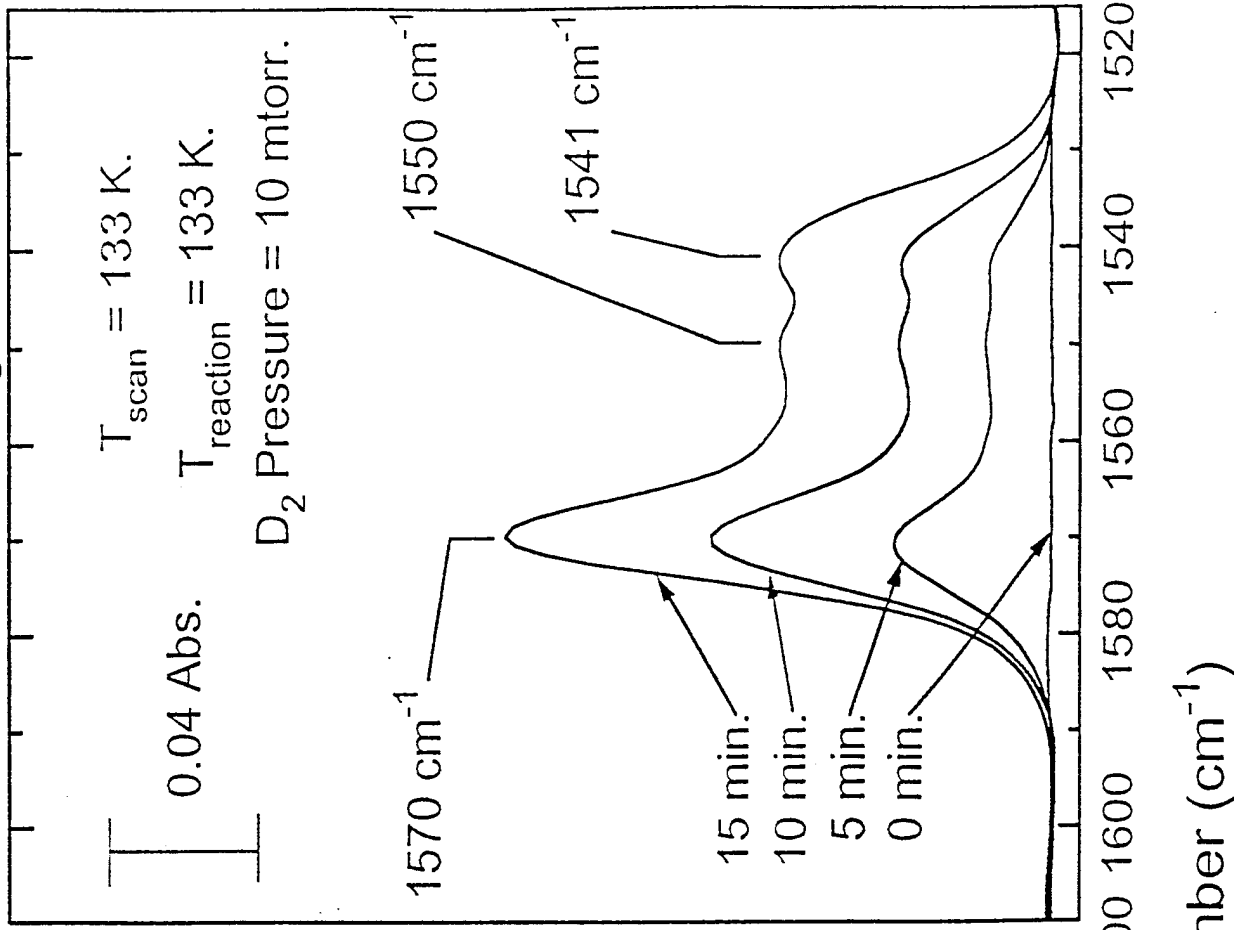


Reaction of D + SiH_x at 133 K.

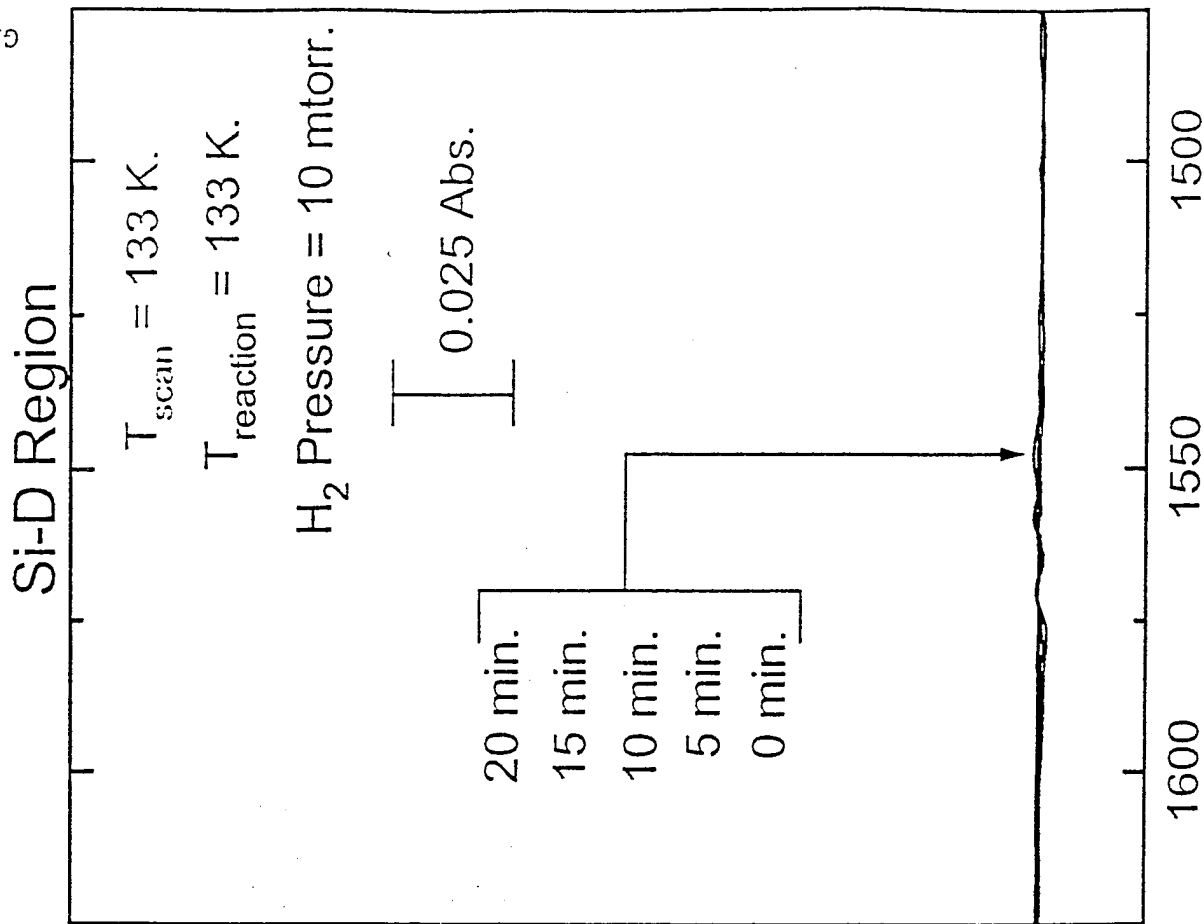
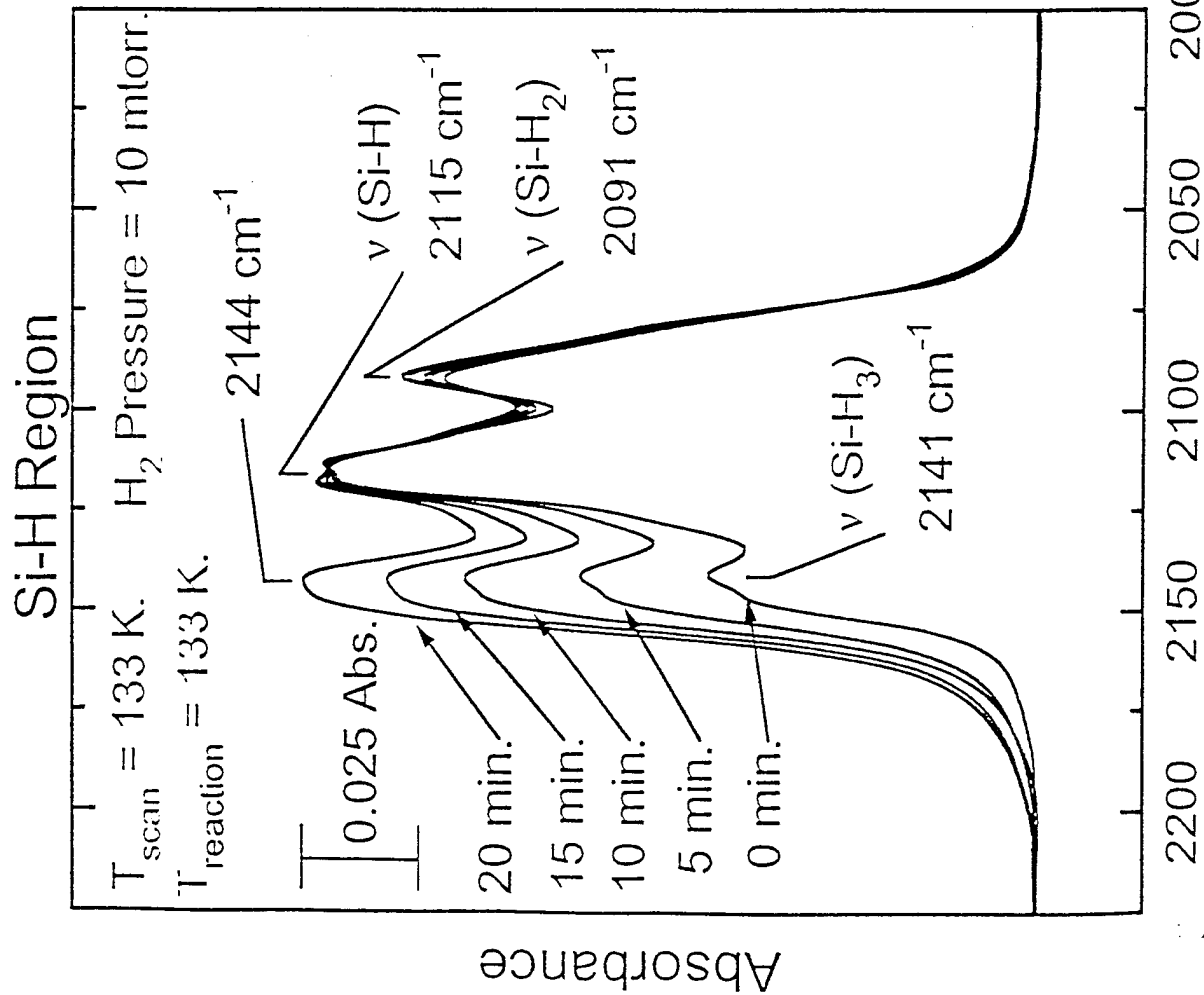
Si-H Region



Si-D Region

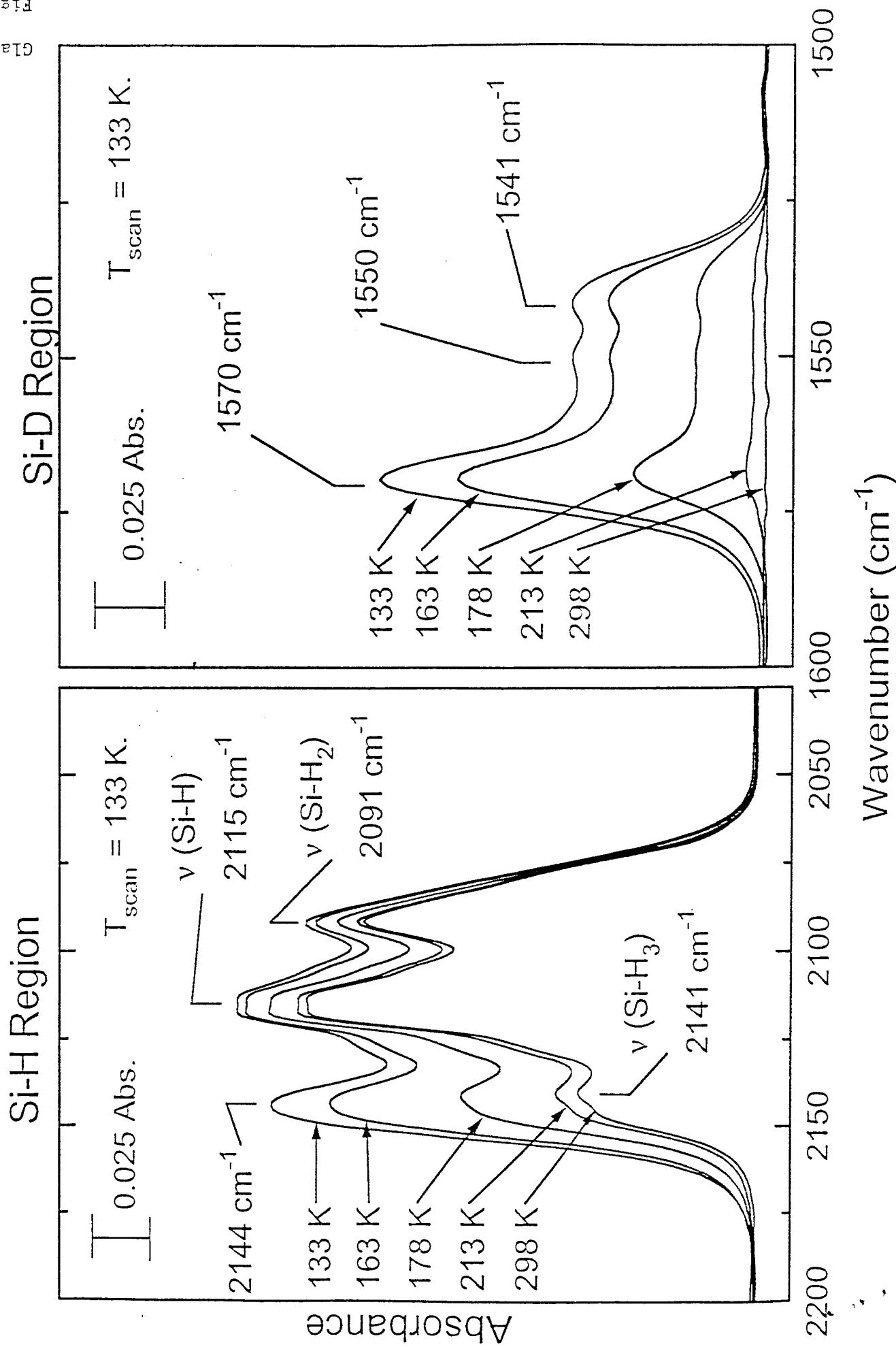


Reaction of $H + SiH_x$ at 133 K.

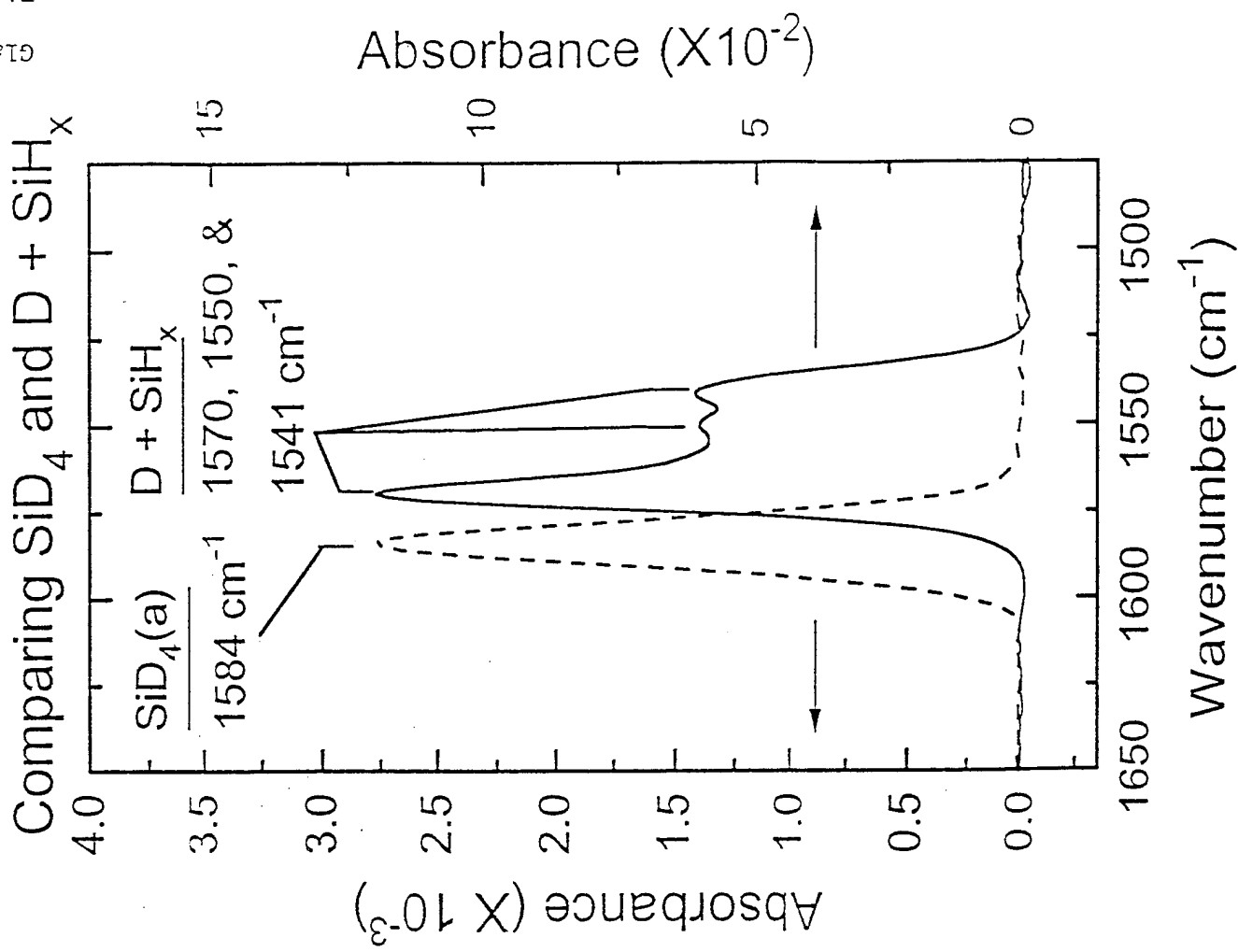
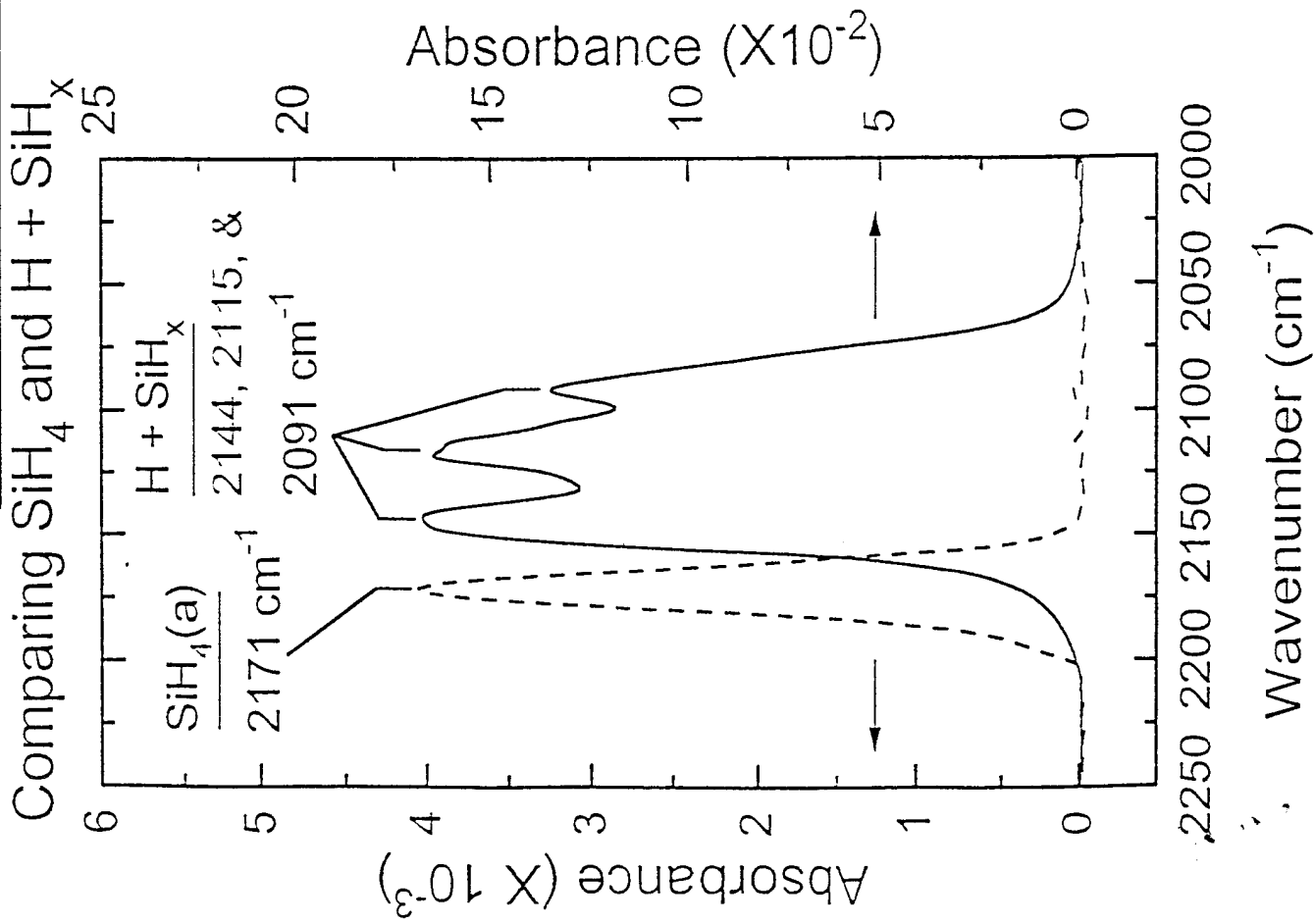


Wavenumber (cm^{-1})

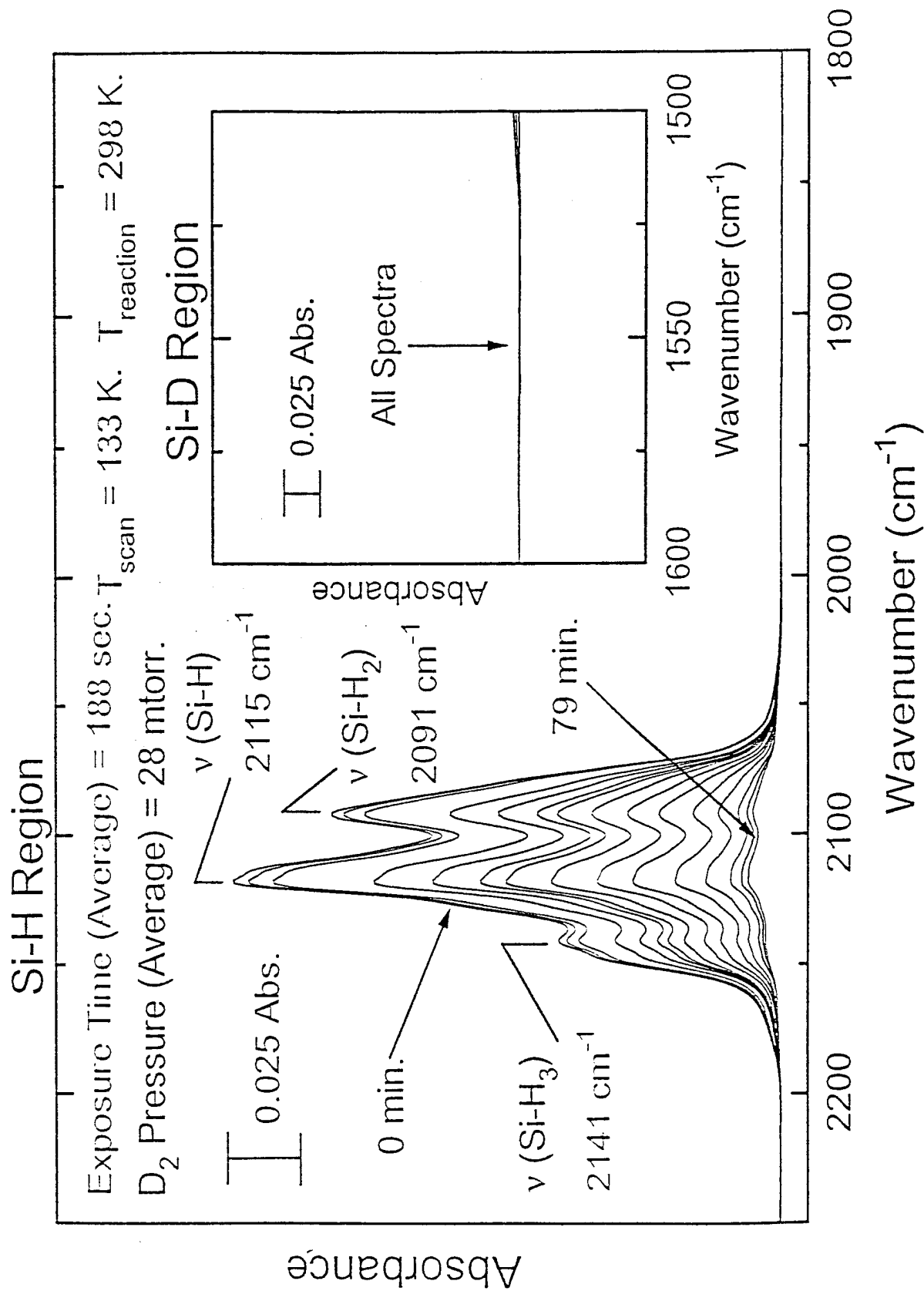
Heating of D + SiH_x Reaction.



Spectral Study of $\text{SiH}_4(\text{a})$ and $\text{SiD}_4(\text{a})$.



Reaction of D + SiH_x at 298 K.



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